

Electronic Properties of Ultra-Thin Aluminum Nanowires

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Abstract

We have carried out first principles electronic structure and total energy calculations for a series of ultrathin aluminum nanowires, based on structures obtained by relaxing the model wires of Gulseren et al [1]. The number of conducting channels is followed as the wires radius is increased. The results suggest that pentagonal wires should be detectable, as the only ones who can yield a channel number between 8 and 10.

I. INTRODUCTION

Conductance quantization in break junctions [2] and tip-surface contacts [3–5] proves the existence of extremely narrow constrictions between bulk conductors. These constrictions can be seen as very short nanowires, for which several models [6–9] and first principle descriptions [10–13] can be found in the literature. In proximity of surface melting, much longer nanowires have been predicted in simulation [14] and found experimentally [15] for Pb. The detailed shape of these long nanowires has not been directly accessible, but simulations showed that they could be extremely thin and regular.

Very recently, Takayanagi and his group were able to demonstrate [16] that very long and regular gold wires of decreasing radius and varying structure can be stabilized, suspended in

vacuum between two tips. While a study for gold, whose wire structure and properties are rather substantially complicated by the presence of s-d interplay [17] and by surface reconstruction phenomena [18,19], we have in the meanwhile carried out a study for a simple s-p metal, aluminum, whose idealized wire behavior can to some extent serve as a prototypical case study.

Actually also data on Al wires have been reported [2,20,21]. Krans and coworkers [2] used mechanically controllable break junctions (MCBJ) to measure the conductance of Al one-atom point contacts at $T = 4.2$ K and found a quantized behaviour with clear plateaux for the smallest integer multiples of $2e^2/h$. Using a similar setup, Scheer and coworkers [20] were able to decompose the total transmission into contributions from various channels. This showed that, even in the case of a single quantum of conductivity, at least three channels were *open* and contributed to the total transport. Balicas et al. [21] found that histograms of conductance measurements, taken at room temperature, show a structure with features around small integer multiples (1,3,...) of the quantum of conductivity $2e^2/h$.

In this work we present realistic Generalized Gradient Approximation (GGA) electronic structure calculations of several wires, and discuss in particular the interplay between structure and number of conducting channels, by comparing our results with the predictions of two simple jellium models: a *hard-wall* cylinder, and a *soft-wall* one with parameters appropriate for the Al surface [7].

The rest of the paper is organized as follows. In Section II we describe the procedures, methods, and approximations adopted for the wire calculations, as well as the physical quantities which will be monitored. Section III presents the resulting electronic structures, total energies, and number of channels for a set of ultra-thin wires of increasing thickness, ranging from monoatomic to hexagonal. In section IV we discuss our results, and possible future calculations aimed at including phenomena beyond the present level of description.

II. METHOD

All calculations presented here are carried out for straight wires, using a supercell technique. The wires are infinite and periodic along the z -direction, and periodically repeated as a square lattice with a very large spacing in the $x - y$ plane.

We have considered altogether 7 different wires with increasing cross section, namely: monoatomic, diatomic, triatomic, centered pentagonal (staggered and eclipsed), and centered hexagonal (staggered and eclipsed). The initial structure for the wires was taken from Gulseren et al.'s glue modeling [1], with the understanding that this should represent no more than a suggestion (glue models are not sufficiently accurate in this thin wire regime) for further ab-initio refinement. Of course this procedure does not ensure an exhaustive enumeration of all possible low-energy, or "magic" thin wire structures. Nonetheless, it does turn out that the glue model nanowires are close enough to well defined local energy minima, so that we believe we have at least a subset of the nanowires which real Al, given the proper experimental conditions, would form.

The effect of strong electron correlations, and of classical and quantum fluctuations, all of which are of course crucial in a one dimensional system, are not included here. In particular, we will not include at this level the possibility of Peierls or spin-Peierls dimerizations, of ferromagnetism, and/or Mott-Hubbard antiferromagnetic insulator states. These well-known phenomena and their mutual competition of course do require more sophisticated approaches. The scope of the present calculations is also to lay the ground with a description of the basic, mean-field metallic state of the wire, upon which these further approaches could be later built.

The electronic structure calculations were performed within the GGA, using the Becke-Perdew exchange-correlation functional [23]. The electron-ion interaction was described by means of a pseudopotential by Stumpf et al. [24], and the wavefunctions were expanded in planewaves up to a cutoff energy $E_{cut} = 12$ Ry.

Within this scheme, bulk Al was calculated to possess a lattice spacing of 3.95 Å (experi-

mental 4.0496 Å), and a cohesive energy of 3.74 eV/atom, (experimental 3.39 eV/atom). We also calculated the Al₂ molecule, which we found correctly to be an electronic triplet with a length of 2.657 Å. For most calculations the **k**-point summation was carried out directly on a regular mesh of 10 **k**-points in half of the one dimensional BZ along k_z , while only the Γ point was used in the $k_x - k_y$ plane. The sampling along k_z was occasionally increased to 50 **k**-points, when especially high accuracy was needed. Stress along the wire direction, supported by the periodic boundary conditions, is evaluated in our code according to the Nielsen-Martin prescription [22], and convergence was assumed when the stress along z was relaxed at around 10 kbar. Atomic relaxations were carried out using the Hellmann-Feynman forces and convergence was assumed when forces fell below ~ 10 meV/Å.

III. RESULTS

The calculated electronic structure for four among the seven wires considered, with atoms in their fully relaxed positions, are shown along with their density of states (DOS) in Fig.1 a-d. All wires are metallic. Not surprisingly, the band structures comprise a number of clear 1D subbands which disperse rather free electron like along the wire. This band dispersion is strongly reminiscent of quantized states in a cylinder; but of course only roughly so, and the detailed atomic structure has a very non-negligible impact. The DOS at E_F jumps without continuity from a wire to another. Needless to say, wires where this quantity is lower will be comparatively more stable against instabilities.

In the ballistic transport regime, the number of bands crossing the Fermi level determines the number of channels open for conduction. The detailed bands do depend substantially upon the underlying atomistic structure of the wire, suggesting that jellium models should be inadequate to describe the detailed physics of real nanowires.

The number of channels (as defined above) decreases with decreasing wire diameter. If we introduce a conventional *wire radius* using, for example, Gulseren et al.'s [1] definition, (a sort of local gyration radius) then we can plot the channel number versus radius, as in Fig.2.

In the same figure we compare our predictions with a hard-wall cylinder jellium model, whose solution are Bessel functions, and with *soft-wall* jellium model [7], whose solutions implies just a rigid translation of the stepped curve, which depends upon the Fermi energy and the work function of the material (for Al we used $E_f = 11.7$ eV and $\phi = 4.28$ eV).

If we note that the hexagonal wire (with 11 channels) is the smallest of the possible *crystalline* fcc wires, we can conclude that any observed conductance plateau which might be traced back to less than 11 channels, is in itself indirect evidence of a noncrystalline wire. In particular, pentagonal (*icosahedral*) wires are predicted to possess 8 or 10 conducting channels, in the eclipsed and the staggered pentagonal wires respectively.

The energy per particle decreases for increasing radius, as expected from size corrections of the type $E(R) = E(\infty) + 2\gamma/R$, where γ is the surface energy. Comparison with the glue model energies is shown in Fig.3. We note that our calculations tend to predict somewhat higher cohesive energies. A fit to this energies, up to the two-fold wire, predicts a surface energy of $\gamma = 45 \pm 5 \text{ eV}/\text{\AA}^2$. The monoatomic wire is observed to lie out of this fitting curve.

IV. DISCUSSION

We have calculated the GGA electronic structure and relaxed total energy of a sequence of ultra-thin aluminum nanowires. Despite its resemblance with the corresponding jellium result, the detailed electronic structure is in fact strongly dependent on the precise atomistic structure. The number of conducting channels has been determined, and it is found that channel numbers below 11 cannot correspond to crystalline wires. In particular, the pentagonal wires discovered theoretically by Gulseren et al. should possess 8 or 10 channels, implying an ideal ballistic conductivity of 8 or 10 times ($2e^2/h$). In future we will consider the eventual transition to (anti-)ferromagnetic states of some of the wires, allowing also for possible dimerizations. This transition might be induced stretching the wire in order to *push* the Fermi level near to a singularity of the DOS, as predicted with a jellium model by Zabala *et al.* [25].

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FIGURES

FIG. 1. Band structures for four different Al nanowires, and relative density of states: (a) monoatomic wire, (b) triangular wire, (c) pentagonal staggered wire, and (d) hexagonal eclipsed wire.

FIG. 2. Number of channels open for conduction. The dashed line is the number of channels predicted for a jellium system confined in a hard-wall cylinder, as computed in Ref. [7]. The dashed line (soft-wall) is the prediction for the same system corrected to better describe a real wire (see text).

FIG. 3. Cohesive energy vs. the inverse of the wire radius. Open symbols correspond to GGA calculations. Filled symbols to classical MD from Ref. [1]. Diamonds correspond to hexagonal wires, squares to pentagonal, up-triangles to triangular, down-triangles to two-fold wires, and the open circle to monoatomic wire. The line is a fit to the formula $E(R) = E(\infty) + 2\gamma/R$ and predicts $\gamma = 45 \pm 5 \text{ meV/\AA}^2$.





